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Development of Radiation Resistant Electrical Cable Insulations¹

B. S. Lee, P. Soo and D. R. MacKenzie

Department of Advanced Technology,
Brookhaven National Laboratory, Upton, NY 11973

ABSTRACT

Two new polyethylene cable insulations have been formulated for nuclear applications, and have been tested under gamma radiation. Both insulations are based on low density polyethylene, one with PbO and the other with Sb₂O₃ as additives. The test results show that the concept of using inorganic antioxidants to retard radiation initiated oxidation (RIO) is viable. PbO is more effective than Sb₂O₃ in minimizing RIO.

INTRODUCTION

The first comprehensive study of gamma radiation damage to insulation and jackets for electrical cables in nuclear reactor systems was conducted by Blodgett[1] two decades ago. In this study, thirteen different kinds of polymer were evaluated up to a total dose of 5×10^5 Gy (5×10^7 rads) at a dose rate of 5×10^3 Gy/h (5×10^5 rads/h). It was estimated that the total radiation dose absorbed by a cable within the commercial nuclear reactor containment area may approach 5×10^5 Gy during an assumed reactor lifetime of 40 years if there were no abnormal bursts of radiation. One of the conclusions drawn from this study was that CSPE (chlorosulfonated polyethylene) or CPE (chlorinated polyethylene) jacketed insulation based on nonfilled CLPE (cross-linked polyethylene) or carbon filled CLPE should last at least 40 years when exposed to a total radiation dose up to 5×10^5 Gy and would still be serviceable after exposure up to 10^6 Gy.

However, in November 1976 an inspection of a pump suction valve motor assembly in the Savannah River K-reactor at Aiken, South Carolina, revealed badly embrittled polyethylene (PE) insulation on the power control wiring. The maximum dose experienced by the cable materials was only 2.5×10^4 Gy during the 12 years of operating life. The subsequent checking of other cables in the C- and P- reactors disclosed additional embrittled cables[2]. This degradation of the cables was faster-than-expected, so Clough and Gillen[2] conducted an extensive investigation of cable degradation by radiation.

The most important finding from the study of Clough and Gillen was that, when oxygen is present, dose rate is another important parameter to consider in addition to total dose in the polymer degradation processes. It was also shown that a strong synergism of radiation and elevated temperature, as well as dose rate, led to unexpectedly rapid degradation of the Savannah River reactor cables. These findings can be explained by the effects of diffusion of oxygen into the cable materials during service which resulted in oxidation processes. Thus, the degradation process for the cable insulation and jacket under radiation can be termed radiation initiated oxidation (RIO).

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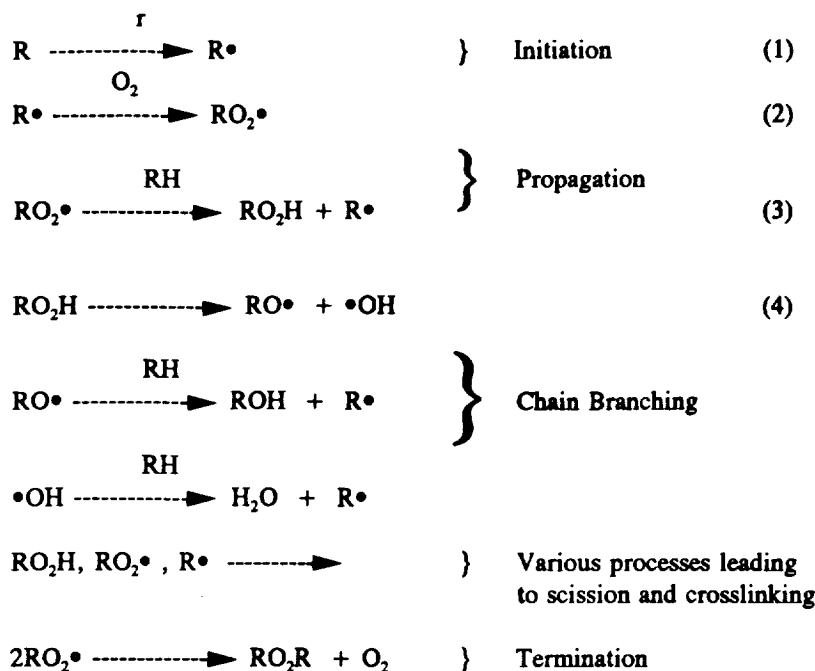
has a delivered energy density of 2.44J/cc (current design by a major capacitor manufacturer), plasma treated PVDF film can raise this value to 3.51J/cc. What is even more significant is that the additional cost for this benefit may be minimal because process and equipment are relatively simple, and if the film is to be metallized, the treatment can be performed inline with the metallization process in the same chamber. Furthermore, the lower wetting angle of the surface of the treated film will improve the capacitor impregnation process and thus reduce air voids that can lead to partial discharges during the operation of the capacitor. Minimization of the partial discharge activity can lead to improved performance and reliability under a broad range of operating conditions.

Although such an increase in energy density and reliability may not satisfy the longer term objectives of several government programs that require capacitor energy densities as high as 10J/cc, plasma treated PVDF represents a significant step in this direction that is relatively easy to attain. In the short term this improvement can benefit several electromagnetic weapon programs, and it can have an impact on commercial capacitor products for applications such as portable defibrillators, flash lamps, and pulse generators.

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The mechanisms for RIO of polymers are fairly well understood [3,4,5], and were summarized by Clough[6] as the following:



For RIO to proceed, both oxygen and free radicals should be present in a polymer. It has been shown that radicals generated in the absence of oxygen largely disappear by recombination and disproportionation reactions and that little degradation occurs [7]. It is generally believed that formation of hydroperoxides by reaction of free radicals with oxygen and breakdown of these hydroperoxides forming more free radicals (reactions 3 and 4 above) are the important processes for the chain reactions of RIO. In attempting to reduce RIO, one could consider adding chemicals to the polymer so that the chain reaction is terminated before hydroperoxide formation. Limited protection of polymeric materials against radiation damage has been achieved by use of additives called "antirads". Generally these antirads work by scavenging, in competition with oxygen, the free radicals formed in the reaction (1) above. So far, most of the additives used have been organic, and the search is still proceeding to find additives that will give longer-lasting protection.

This study was initiated to find inorganic additives which would interrupt the chain reaction by reacting with free radicals formed in reaction (2). Thus, the objectives of the current study were twofold; one was to check the concept of adding inorganic additives to consume oxygen containing free radicals thereby retarding RIO, and the other was to develop a polymer insulation material which will have prolonged service life utilizing this concept [8].

DEVELOPMENT STRATEGY

To react with oxygen containing free radicals, inorganic reducing agents can be used as additives. These would include, besides certain elements such as carbon, salts with cations in the reduced state, salts with reducing anions, or salts with both. Some of the cations and anions of interest include:

- a) Low valence states of the transition elements, e.g., Fe^{2+} , Mn^{2+} , Cr^{2+} , Co^{2+} . They might be used as oxides or as salts such as sulfates, phosphates, or possibly chlorides.
- b) Group V cations in the reduced state, e.g., As^{3+} , Sb^{3+} and Bi^{3+} . (Arsenic, however, is not recommended).
- c) Group IV cations in the reduced state, e.g., Pb^{2+} .
- d) Reducing anions which might be useful are sulfite, selenite, and phosphite.
- e) The reduced form of a cation could possibly be used as a salt with a reducing anion.

Choice of Additives

Among the cations listed above, the transition elements in a) may not be a good choice, since it was reported that some of these ions operate as catalysts in the autoxidation of certain polymer systems[9,10,11]. As shown in the above list, several other additives could have been tried for this study. However due to the limitation on resources, only two additives were selected, Sb_2O_3 and PbO . Rockbestos Company in Connecticut agreed to assist us in our work primarily by preparing the new polymer formulations.

Choice of Polymer

Currently, PVC and low density polyethylene (LDPE) are widely used for cable insulation and jackets due to their good extrudability combined with good insulation properties. These materials also show acceptable radiation resistance, and a fair amount of data on radiation effects on these is available. High density polyethylene (HDPE) is less radiation resistant than LDPE at both high and low dose rates; PVC is more sensitive to dose rate effects than LDPE[6]. Thus, LDPE was chosen as the base polymer for this study.

EXPERIMENTAL

As shown in Table 1, LDPE with seven different compositions were molded into sheets of 15 cm x 15 cm x 0.17 cm. The seven compositions are a LDPE control without additives, and LDPE with two different additives at three different concentrations.

Dogbone shaped samples (gauge length: 3.4 cm, width: 0.6 cm, thickness: 0.17 cm) were stamped from the sheets using a hydraulic press and an ASTM recommended die. A batch of 14 samples (two for each composition) were stacked together with spacers between them. The samples were degreased with alcohol before irradiation.

The gamma irradiation facility at Brookhaven National Laboratory (BNL) was used to irradiate the specimens in air at 10°C. Three different dose rates were used for this study: 3.31×10^3 , 6.26×10^3 and 1.1×10^4 Gy/h. The total doses used ranged from 1.3×10^6 Gy and 5.37×10^6 Gy.

An Instron tensile testing machine was used to measure elongation and tensile strength. A displacement rate of 5 cm/minute was used. A 2.5 cm gauge was marked at the center of the sample, and the distance between the gauge marks was followed until the sample broke.

TABLE I
Compositions of Test Samples

Sample ID	Composition (weight %)
A	LDPE homopolymer + 1% PbO
B	" + 1% Sb ₂ O ₃
C	" + 3% PbO
D	" + 3% Sb ₂ O ₃
E	" + 10% PbO
F	" + 10% Sb ₂ O ₃
Z (Control)	"

RESULTS

At the highest dose rate used, 1.1×10^4 Gy/h, samples A - D behaved very similarly to the control sample. Samples E and F seem to have slightly higher elongations compared to the control samples up to the total dose of 5×10^5 Gy, but the differences may not be significant.

At a dose rate of 6.26×10^3 Gy/h, all six samples showed improvements in elongation over control samples up to a total dose of 3×10^5 Gy, with the PbO containing samples, A, C and E outperforming the Sb₂O₃ added samples, B, D and F. At total doses higher than 5×10^5 Gy, all six samples behaved similarly to the control samples. Among the samples with the same kind of additive, the higher the concentration, the more distinct the improvement.

At a dose rate of 3.31×10^3 Gy/h, for the PbO containing samples, only sample E (10% PbO) showed improved elongations compared with the control sample up to the total dose of 1.6×10^5 Gy. It seems that all three Sb₂O₃ containing samples, B, D and F showed slight improvements in elongation over the control samples up to a dose of 1.6×10^5 Gy.

It should be mentioned that the addition of PbO to PE reduces the ductilities, i.e., elongations of the unirradiated samples decrease significantly as shown in Fig. 1. Thus, the real effects of the additives as antioxidants may be shown better if the elongation data are normalized to the elongations of the unirradiated samples. In Figures 2 - 5, the elongation values were averaged, and normalized to those of unirradiated samples. The same trends as discussed earlier can be seen in these plots except that the rankings of performance are switched in some cases. Again, more data are needed to draw firmer conclusions regarding the optimum composition.

From these plots, the effects of the additives may be roughly estimated in terms of total dose at which the elongation is reduced to half of its original value. For PbO added samples (Fig. 2), at a dose rate of 6.26×10^3 Gy/h, it takes about 40 % more total dose for the elongation to be reduced to half of its original value. In other words, at this dose rate, it takes 40 % longer time for the PbO added samples to reach half of the original elongation. At dose rates of 1.1×10^4 Gy/h and 3.31×10^3 Gy/h (Fig. 3 and 4), it takes 39 % and 30 % more time for the PbO added samples to reach half of the original elongations, respectively. As discussed earlier, for Sb₂O₃ added samples the effects are not as significant. For instance, at 3.31×10^3 Gy/h (Fig. 5), it takes 7 % more time for the elongations of Sb₂O₃ added samples to be reduce to their original values.

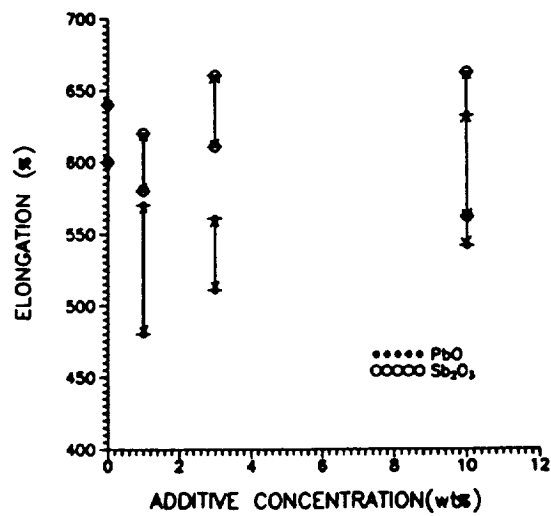


Figure 1. Elongation for unirradiated samples with different additive concentrations.

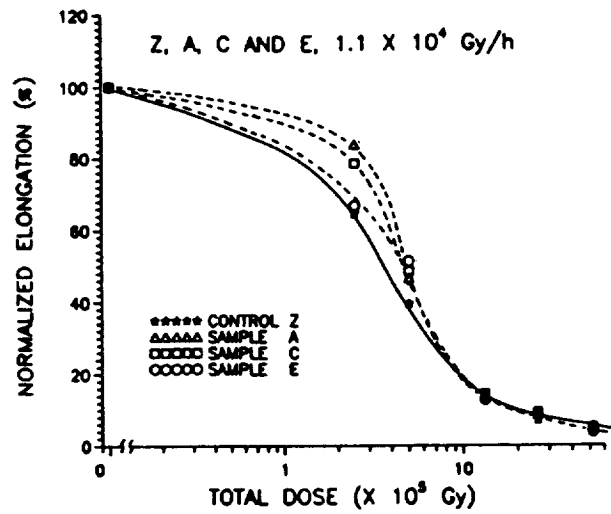


Figure 2. Normalized elongation for samples Z, A, C, and E irradiated at a dose rate of 1.1×10^4 Gy/hour.

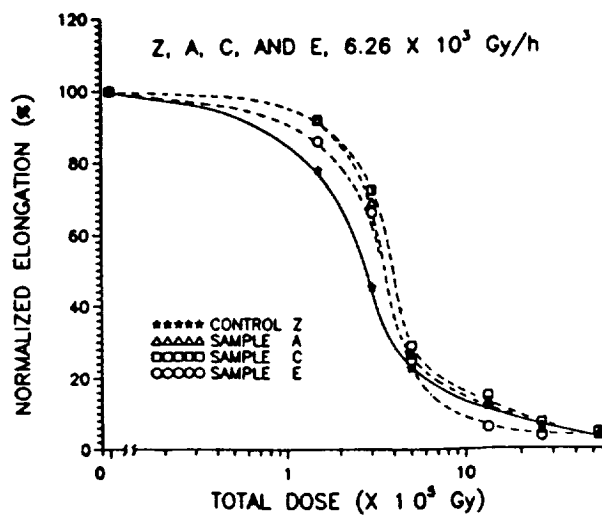


Figure 3. Normalized elongation for samples Z, A, C, and E irradiated at a dose rate of 6.26×10^3 Gy/hour.

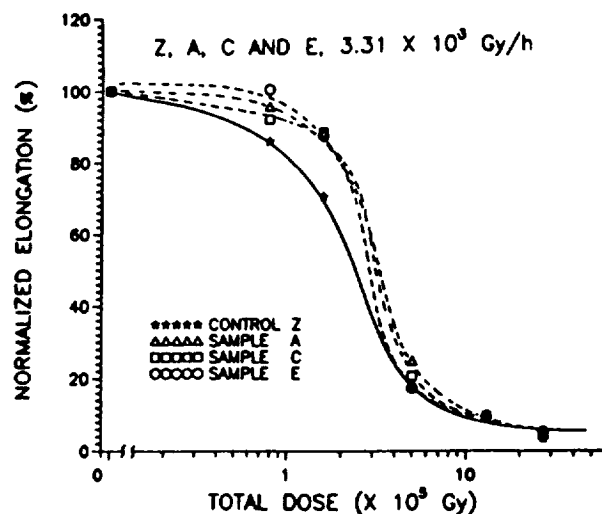


Figure 4. Normalized elongation for samples Z, A, C, and E irradiated at a dose rate of 3.31×10^3 Gy/hour.

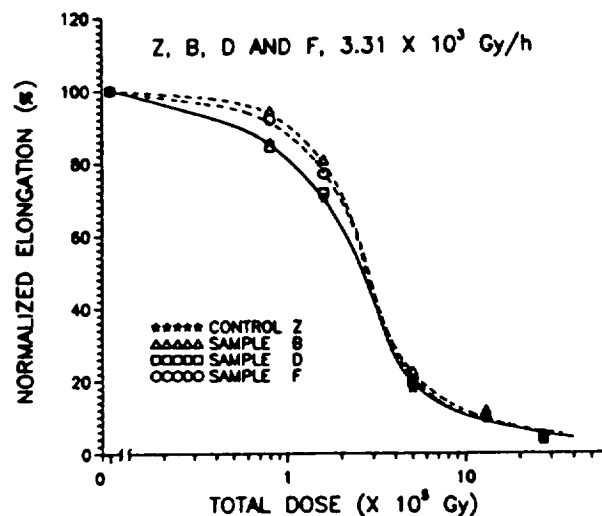


Figure 5. Normalized elongation for samples Z, B, D, and F irradiated at a dose rate of 3.31×10^3 Gy/hour.

Based on these results, it is believed that PbO works effectively as an antioxidant until the total dose reaches a certain level which is determined by the dose rate used and the amount of additive. For instance, at 6.26×10^3 Gy/h, for total doses higher than 3×10^5 Gy, the addition of PbO did not make much difference. For a dose rate of 3.31×10^3 Gy/h, the PbO addition to the samples A (1%) and C (3%) does not seem to be effective in slowing down RIO for the range of total doses used in this study, and only the sample E showed improved elongations up to a dose of 1.6×10^5 Gy.

Addition of Sb_2O_3 seems to improve the elongation slightly for all the three dose rates used. However, the degree of improvement is not as much as that for PbO.

DISCUSSION

These observed improvements of elongation properties may be attributed to one of the following mechanisms:

- a) the inorganic additives reacted with oxygen-containing free radicals and retarded RIO.
- b) the inorganic additives reacted with free radicals and retarded RIO.
- c) the inorganic additives worked as energy sinks.

It may also be possible that the additives, which in the ground state do not react with oxygen, became electronically excited and reacted with oxygen. Within the scope of this study, it is not possible to provide information which can determine exactly how the additives worked. However, due to the reduced state of the cations of the additives, it is believed that these additives retarded RIO by reacting with oxygen-containing free radicals.

Based on the RIO mechanisms discussed earlier and an assumption that the inorganic additives improved elongation properties by reacting with oxygen in polyethylene (PE), what follows is an attempt to explain the experimental results.

It is generally believed that the degradation inside a polymer is not homogeneous when oxygen diffusion is involved. Clough and Gillen[12] reasoned that, after the initially-dissolved O_2 is used up, a steady-state situation will result in which strong oxidation occurs near the edges and degradation may proceed in the absence of oxygen or at reduced oxygen concentrations in the interior regions.

As oxygen molecules diffuse in from the surface, they react with free radicals generated by radiation, and the oxygen concentration in the polymer will decrease with depth from the specimen surface. Also, there may be a certain distance from the surface beyond which the oxygen concentration is negligible. For a polymer exposed to a high dose rate radiation in air, oxygen diffusion depth, L , should be shallow since the free radical concentration in the polymer should be high. In other words, oxygen molecules are consumed by free radicals before they diffuse to an appreciable depth. On the other hand, for the case of a low dose rate radiation, L should be large. Thus, the oxygen profiles as a function of the distance from the polymer surface may be represented schematically as shown in Fig. 6 (a) for polymer samples exposed to high, medium and low dose rate radiations in air.

RIO will proceed mainly in the area where oxygen is available, which will result in different oxygen diffusion depths for different dose rates for the same total dose: L_1 , L_2 and L_3 for low, medium and high dose rate, respectively. Assuming that ductility, i.e., elongation is determined primarily by the amount of unoxidized polymer, these oxygen profiles (or oxidation profiles) may explain why the polymer irradiated at higher dose rate shows higher elongation (less radiation damage) than that irradiated at lower dose rate when the total doses absorbed are the same (dose rate effect).

The above argument on heterogeneous oxidation may be used to explain the effects of additives used in this study. The role of an additive is to reduce the oxygen concentration, so the effects of an additive on the oxidation profile of a polymer should be similar to those of free radicals. In other words, the difference between the profiles of a polymer with an additive and the one without should be similar to those between polymers irradiated at a high dose rate and a low one as shown in Fig. 6 (b).

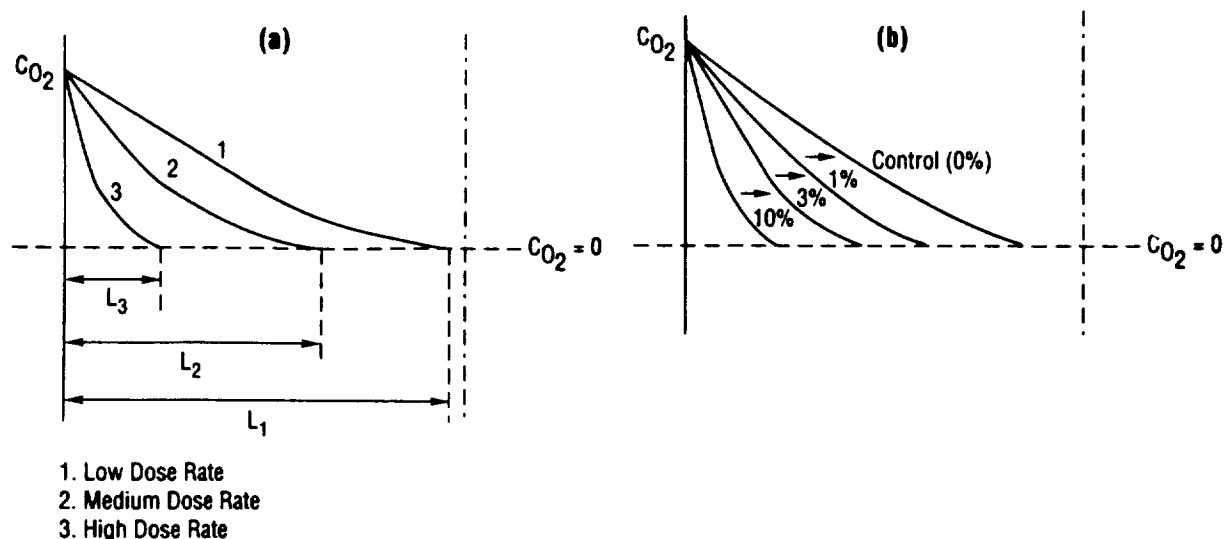


Figure 6. (a) Oxygen concentration profiles for different dose rates.
(b) Oxygen concentration profiles for different amount of additives.

After a certain period of time (or total dose) the additives within the oxidation layer will be consumed or their effectiveness will decrease, and the oxygen concentration profile will move in the direction shown by the arrows in Fig. 6 (b). Thus, the polymer samples with smaller amount of additives, for example, 1% and 3% PbO, will show improvements in elongation over the control sample up to a certain total dose (which is less than 8×10^4 Gy for dose rate of 3.31×10^3 Gy/h), after which these polymers will behave the same as the control sample. For the 10% PbO sample, a higher total dose is needed for the additives to lose effectiveness. The oxidation profile for 10% PbO shown in Fig. 6 (b) should move in the direction shown by the arrow as the total dose absorbed by the sample increases, until the sample behaves similarly to the control sample. Figure 3 shows that the additives were effective for the 10% PbO sample at least until the total dose reached 2×10^5 Gy at a dose rate of 3.31×10^3 Gy/h.

SUMMARY AND CONCLUSIONS

Two new polyethylene cable insulations have been formulated for nuclear applications, and preliminary tests have been completed under gamma radiation. Both insulations are based on low density polyethylene, one with PbO and the other with Sb_2O_3 as additives.

The following conclusions may be drawn from this study:

- The concept of using inorganic antioxidants to retard radiation initiated oxidation (RIO) is viable.
- PbO is more effective than Sb_2O_3 in retarding radiation initiated oxidation.
- Further comprehensive testing will be needed, if such formulations are to be fully qualified for nuclear applications.

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